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Model Filled Polymers I. Synthesis of Crosslinked Monodisperse Polystyrene Beads

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Monodisperse crosslinked polystyrene beads of varied size and crosslink density are prepared by emulsion copolymerization of styrene and divinylbenzene in the absence of emulsifier. Tumbling and internally stirred reactors were used for synthesis, with minimal agglomeration at at least 0.22 weight percent potassium persulfate and up to 10 percent by weight of styrene in aqueous emulsion in the absence of oxygen. Particle sizes decreased from 800 to 200 nm on raising the polymerization temperature from 60 to 95°C. The glass transition temperature of the beads increased from 104.4 to 133°C by the inclusion of up to 10% by weight of divinylbenzene. The thermal stability of the beads was higher for peroxide than for persulfate initiation. The crosslink density estimated from the degree of swelling was about one third that expected from stoichiometry. The polystyrene beads are used as filler particles in polymer composites.

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Model Filled Polymers I. Synthesis of Crosslinked Monodisperse Polystyrene Beads

Filled polymer systems are of enormous technological importance. The rubber industry depends on the incorporation of substantial amounts of filler in order to reinforce elastomers. Commercial plastics result from the ability of fillers to impart useful properties to polymers. The design of advanced composites is based on the skillful selection and processing of fillers in continuous matrices. In spite of the ubiquity of filled polymer systems, the fundamental mechanisms by which filler particles modify the properties of polymers are poorly understood, largely because of ill-defined filler morphology and the complex nature of filler/polymer interactions [1-9]. In order to investigate the fundamental principles underlying the effects of fillers in polymeric systems, researchers have designed and studied filled systems involving model particles, such as glass [10-16] and aluminum [17] spheres.

In recent years, procedures have been perfected for preparing spherical polymer particles of uniform size [18-20]. In research work spanning more than two decades, Ottewill explored and defined experimental conditions for the emulsion polymerization of monodisperse polystyrene beads. Early research concerned aspects of colloid chemistry, surfaces and interfaces, the stabilization of dispersions by surfactants and the structure of microemulsions and micelles [21-26]. Filler/matrix interactions were explored for a variety of systems [27-29]. Light scattering from dispersions of monodisperse polystyrene latexes

were analyzed [30]. Moreover, a series of papers were published on the preparation and characterization of monodisperse polystyrene latexes [31-33]. Most of this research involved the use of various emulsifiers and initiators [34] and attention was directed at characterizing the particle surface [35]. Ordinarily, it is very difficult to remove surface active agents adsorbed on the particles. Accordingly, the emulsion polymerization of polystyrene was pursued in the absence of emulsifier [36,37]. Under such conditions, surface properties are controlled by the choice of initiator [34]. Using persulfate initiator, latex particles were stabilized by functional groups, primarily sulfate, bound to the surface [38]. It has been proposed that surface active oligomeric free radicals formed during polymerization stabilize the micelles in an emulsifier free emulsion polymerization [38]. Indeed, particles formed initially (at very low conversion) consisted largely of very low molar mass polystyrene.

We have suggested that monodisperse polystyrene beads with defined surfaces would be a well characterized filler for elucidating filler/polymer interactions. In order to control the properties of such beads, we prepare monodisperse crosslinked polystyrene beads of varied size, crosslink density and surface composition. In this paper, we describe several techniques for bead preparation and report on the kinetics of polymerization and particle growth. Techniques for characterizing the beads are reported, as well.

EXPERIMENTAL DETAILS

MATERIALS

Styrene monomer and divinylbenzene crosslinker are products of Aldrich Chemical Company. Styrene is 99% pure and inhibited by 10-15 ppm 4-tertiary-butylcatechol (4-TBC). Divinylbenzene consists of a mixture of 55% meta and parasomers, 42% ethyl vinyl benzene and 3% diethylbenzene, which is inhibited with ~1000 ppm 4-TBC. Styrene and divinylbenzene are stored at 5°C. The monomer and crosslinker are washed with an equal volume of an aqueous solution of 10% sodium hydroxide for four times, followed by deionized

water for four times, in order to remove the inhibitor before polymerization. Potassium persulfate and hydrogen peroxide (30% aqueous solution), initiators, sodium hydroxide and sodium chloride are certified Fisher Scientific products. Deionized water for polymerization and washing is purified water from Sparkletts. Methanol is purchased from EM Science and dry nitrogen from MG Industries Gas Products.

POLYMERIZATION

Tumbling Reactor

Purified styrene, divinylbenzene and water are added to a one liter glass bottle and purged by bubbling nitrogen for 15 minutes. The ratio of styrene to water is typically 10% by volume. The amount of divinylbenzene is varied from 0.1 to 10% by weight of styrene. Initiator, usually 0.22 weight % potassium persulfate, based on styrene, is added, the bottle sealed and the contents thoroughly mixed. Bottles are mounted on a motor driven device which rotates the bottles end over end at constant speeds between 15 and 45 rpm. Most runs are conducted at 30 rpm. The entire assembly is thermostated in a large water bath with temperature controlled to ±1.0°C. Polymerization is conducted at selected temperatures between 60 and 95°C for about 20 hours. After reaction, bottles containing polymer are cooled in a freezer, the contents warmed to room temperature and filtered to remove any large agglomerates, and the resultant latex diluted with methanol and centrifuged. The wet solid is isolated and dried in a vacuum oven at 55°C for 24 hours, yielding a fine white powder.

Internally Stirred Reactor

Polymerizations are also conducted in a one liter resin reaction flask, while stirring with a one inch diameter stainless steel paddle stirrer. The flask is fitted with a nitrogen inlet, and a water-cooled condenser, with a wash-bottle trap to prevent back-contamination by air. A typical recipe includes 70 grams styrene plus divinylbenzene, 700 grams water, and 0.160 grams ($0.845 \times 10^{-3} mol/dm^3$) potassium persulfate.

At the beginning of the reaction, small amounts of sodium hydroxide are added to adjust the pH to about 7. Again, the ratio of divinylbenzene to styrene is varied from 0.1 to 10%. In earlier runs, sodium chloride was added to control the ionic strength.

650g of water are added to the reaction flask and the flask placed in a thermostated water bath at selected temperatures between 60 and 95°C. Nitrogen is bubbled through the water and the flow continued throughout the reaction. The stirrer is started and the agitation speed selected. Typically, the stirring speed is adjusted to 350 rpm. After 15 minutes, prewashed monomer and crosslinker are added to the flask and allowed to mix for 20 minutes to equilibrate. Then, potassium persulfate initiator, dissolved in 30 ml. of water is added and washed in with another 20 ml. water. Polymerization occurs at constant temperature for several hours. The polymerization medium may be sampled to assess bead size and conversion.

At conversions exceeding 90%, the reaction flask is removed from the bath, the contents emptied into a bottle and allowed to stand for five minutes. Unreacted monomer often rises to the surface and may be removed. The latex of polystyrene beads in water is cooled to -15°C for one hour and stored at 5°C. The latex is filtered through glass wool to remove any coagulated material and the polystyrene beads recovered as previously described.

Alternatively, the filtered latex is frozen at -15°C for 12 hours and melted at room temperature. After melting, the latex separates into two phases. Solid crosslinked polystyrene beads settle to the bottom and the top layer of clear water is removed. The beads are washed repeatedly with distilled water and with methanol. Beads are removed by normal sedimentation or by filtration and dried in a vacuum oven at 55°C for 24 hours.

In order to measure the variation of conversion with time, two ml. aliquots are removed from the reactor at selected intervals. Samples of polystyrene beads are isolated, washed with methanol and dried at 55°C to constant weight.

CHARACTERIZATION

Scanning Electron Microscopy

For particle size studies, polystyrene latex is diluted with an equal volume of methanol, a drop of the mixture placed on a cover glass and dried in clean air at room temperature. The cover glass is attached to an aluminum sample holder. Dried beads are coated with ~200Å of gold and palladium using a sputter coater and examined with a Cambridge Stereoscan model 360, scanning electron microscope, at magnifications from 10^3 to $7x10^4$. In general, the incident electron beam is normal to the film surface.

Differential Scanning Calorimetry

Glass transition temperatures (Tg) were determined with a differential scanning calorimeter (DSC-4, Perkin-Elmer) which is repeatedly calibrated with indium standards. Samples were heated to 200°C for 2.5 minutes and quenched to 50°C. After 3 minutes, samples were heated from 25 to 200°C at 10°C/min. Tg was identified as the midpoint of the endothermic displacement between linear baselines.

Thermogravimetric Analysis

Thermogravimetry (TGS2, Perkin-Elmer) was run at a heating rate of 10°C/min in air or nitrogen to determine the thermal stability of polystyrene beads.

X-ray Photoelectron Spectroscopy

The surface of polystyrene beads was analyzed by X-ray photoelectron spectroscopy (VG Scientific ESCALAB MKII instrument) using the Mg Kα line (1253.6eV).

Elemental Analysis

Elemental analysis of 2% crosslinked polystyrene beads was done by combustion (Controlled Equipment Corporation 240XA at 970°C) by Oneida Research Services.

Degree of Crosslinking

The degree of crosslinking was estimated by measuring the hydrodynamic radius by dynamic light scattering (DLS) of crosslinked beads swollen to equilibrium in

tetrahydrofuran. DLS was accomplished with an Ar ion laser light source (Spectra Physics 2020-3), a goniometer (Brookhaven Instruments, BI-200SM) for scattering from 10 to 150°C and a photon autocorrelator (Brookhaven Instruments, 2030). Experimental details for this system have been reported [39,40]. From decay of the correlation function, the diffusion coefficient was determined and the size of the crosslinked beads derived.

The degree of swelling was determined by comparing the size of swollen beads from DLS to that of the corresponding dry beads from scanning electron microscopy. The crosslink density was derived by several methods [41-44].

RESULTS

With reasonable care to eliminate oxygen in either polymerization technique described, very little agglomerated material results and polystyrene beads are produced that are extremely monodisperse in size, by scanning electron microscopy (Figure 1). In the absence of divinylbenzene, monodisperse beads increase monotonically in size with increasing conversion (Figure 2). A similar increase in size occurs, as well, in the presence of divinylbenzene. With various ratios of divinylbenzene, up to 10% weight fraction, the average particle size for beads prepared with persulfate initiator at 80°C, varied from 425-455 nm, for a standard formulation. Within experimental error, particle sizes are independent of crosslink density. However, polymerization rates increased with increasing fraction of divinylbenzene [cf. 45]. Excessive reaction rates lead to agglomeration and deviations from monodispersity in size. At 10% divinylbenzene, in order to obtain a high yield of monodisperse beads, the initiator concentration had to be reduced to slow down the rate of polymerization. Moreover, the rate of polymerization had to exceed a minimum value to attain monodisperse sized beads and to minimize agglomeration. For persulfate initiated polymerization at 60°C, the initiator concentration had to be doubled to optimize the yield of monodisperse beads.

The adjustment of ionic strength by the addition of sodium chloride was found to be detrimental for control of monodispersity.

In the tumbling reactor, polystyrene bead size was not affected by rotational speeds from 15 to 45 rpm. However, the amount of agglomeration in the tumbling reactor exceeded that for internal stirring at 350 rpm. Polymerization, with internal stirring in a resin flask, was carried out with different stirrer designs and speeds. Use of a variety of stirrer designs did not effect changes in particle size. Accordingly, internal stirring was routinely conducted with a three bladed stainless steel stirrer (Cole-Palmer N-04553-60). Polymerization was studied at stirring speeds from 200-650 rpm at 80°C. Conversions and particle sizes increased slightly from 200 to 350 rpm, but remained almost constant, thereafter. Above 350 rpm, conversions decreased slightly and further agglomeration occurred at 650 rpm. An agitation rate of 350 rpm was selected for all runs.

Preparations of crosslinked polystyrene latexes with 1.0% (by weight) divinylbenzene were carried out at selected temperatures between 60 and 95°C, at constant monomer, crosslinker and initiator concentrations, in both polymerization configurations. As expected, the conversion increased rapidly with temperature. Figure 3 illustrates results with internal agitation at these temperatures. Corresponding particle sizes decreased with increasing polymerization temperature (Figure 4). Conversions and particle sizes are also, apparently, sensitive to monomer concentration. Using 1% divinylbenzene at 80°C and constant initiator concentration, corresponding conversion and particle size, after polymerization with internal stirring, are illustrated in Figure 5 for several monomer concentrations. The conversion rate increased and the particle size decreased with decreasing monomer concentration. However, the absolute weight of polymer formed at several times was almost independent of monomer concentration. When the monomer content was increased so that the ratio of monomer/water equalled 20%, the emulsion coagulated at low conversion. The ratio of monomer/water was kept below 10%, in order to produce good quality latexes. Polymerization at 95°C, at the lowest monomer/water ratio

(2.5%), yielded beads with an average particle diameter of 181 nm. Polymerizations were also conducted at 80°C at persulfate (initiator) concentrations from 0.423 - 3.38 $x10^{-3}$ mol/dm^3, at constant monomer concentrations for 0 and 1% divinylbenzene. Conversions for 1% divinylbenzene are shown in Figure 6 and particle size data tabulated in Table 1.

From differential scanning calorimetry, the glass transition temperature of the 0.45 μm beads determined for various crosslink density is shown in Table 2.

The X-ray photoelectron spectrum of polystyrene beads, crosslinked with 2% divinylbenzene, indicated that, within experimental error, no oxygen or sulfur are present on the bead surface. Elemental analysis of these beads showed 92.26% carbon and 7.78% hydrogen, essentially the composition of polystyrene.

The thermal stability of polystyrene beads was evaluated by weight loss measuremetns at controlled temperatures (TGA). In nitrogen atmosphere, there was little difference in stability between beads initiated with potassium persulfate or hydrogen peroxide. However, in an air atmosphere, beads initiated with hydrogen peroxide were more stable than beads prepared with persulfate initiation, showing a 17°C increase in the onset of thermal decomposition.

The hydrodynamic radius of swollen polystyrene beads, synthesized with 5% divinylbenzene was 700 nm, compared to 425 nm in the dry state (SEM). The average crosslink density was 1.50 mole percent.

DISCUSSION

The preparation of polystyrene beads that are monodisperse in size, without agglomeration, requires a delicate balance among the rates of initiation, micelle formation, chain propagation and the diffusion of monomer to the growing bead. In the absence of emulsifier, oligomeric free radicals, formed by reaction between polar radical fragments from the initiator and styrene molecules, stabilize polystyrene particles, swollen with styrene

monomer [38,46]. In agreement with reports in the literature [38,47], size exclusion chromatography, in our laboratories, confirms the presence of low molecular weight oligomers in the polymerizing medium, before apparent bead formation. The concentration of such oligomers decreased with conversion. Since bead size increased monotonically with conversion, it is likely that the number of growing particles remains constant during polymerization. However, from size exclusion chromatographic studies on the growth of uncrosslinked beads, we have seen that a gaussian distribution of molecular weights is progressively displaced to higher molecular weight with increasing conversion. A growth in molecular weight with conversion has been reported [48]. We infer an increase in the mean lifetime of propagating chains, with increasing conversion. The fractional surface area associated with each bead may remain constant, as the beads grow in size. Therefore, it is possible that termination by radical recombination may become less efficient, leading to increased molecular weight. One possibility is that oligomeric free radicals are adsorbed onto the surface of growing particles. As the beads increase in size, these free radicals are further separated and persist for longer periods of time, leading to increasing molecular weight.

It appears that in order to avoid agglomeration and ensure a high yield of monodisperse beads, it is necessary to adjust the rate of polymerization, primarily by controlling the initiator concentration. Thus, at high concentrations of a reactive comonomer, divinylbenzene, we had to reduce the concentration of persulfate initiator, while, for polymerization at 60°C, we doubled the initiator concentration. Since the rate of polymerization is sensitve to the initiator concentration, or the concentration of initiating free radicals, we had to eliminate oxygen, which scavenged the free radicals.

Mixing in the tumbling reactor was, apparently, adequate to effect the formation of monodisperse beads over a range of rotational speeds, although some agglomeration was unavoidable by this technique. Internal stirring in a resin flask was found to be more efficient

and controllable, particularly, at a stirring speed of 350 rpm. Agglomeration may result from non-uniformities in the mixing pattern.

As expected, growth rates and bead size are sensitive to polymerization temperture. Indeed, the control of particle size was, largely, effected by choosing the polymerization temperature. In addition to determining the rate of initiation, the temperature of polymerization affects the equilibrium monomer concentration in the aqueous medium surrounding the growing beads [49]. Apparently, as this monomer concentration is increased, by raising the temperature, more emulsifying oligomer is formed and more, but smaller, growing polymer particles result. Thus, the particle diameter decreased from 800 to 200 μm, as the polymerization temperature is raised from 60 to 95°C.

Variations in overall monomer content have little effect on the actual monomer concentration in water, which is primarily determined by reaction temperature. However, the absolute monomer content determines the apparent rate of reaction and the final bead size, as the monomer supply to the growing bead is eventually depleted. Although, the rate of reaction appears to increase with decreasing monomer content (Figure 5), the absolute weight of monomer polymerized was independent of monomer content. Thus, the rate of polymerization was actually constant, but as the monomer content was reduced, the fractional conversion to polymer increases. This indicates that the monomer concentration in solution was independent of overall monomer content. As in typical emulsion polymerization, large monomer droplets act as reservoirs of monomer for bead growth. Indeed, the cube of the particle size in Figure 5, is approximately in the same ratio as monomer concentration. However, the ratio of monomer to water was kept at about 10%, in order to produce good quality latexes. At higher monomer contents, excessive crowding of growing swollen beads may occur, leading to agglomeration at high conversion.

Variations in initiator concentration has small effect on particle size (Table 1), but markedly increases the rate of reaction (Figure 6). If the initiator concentration were too low, the concentration of oligomeric free radicals was inadequate to stabilize the emulsion

and emulsion polymerization stopped at "low" conversion. Higher concentrations of initiator lead to a larger concentration of growing chains, giving a higher rate of polymerization. This is similar to the effect of increasing the polymerization temperature, while keeping the soluble monomer content constant. Apparently, the number of micelles and growing beads, remain approximately constant. This suggests that the number of micelles is sensitive to the actual monomer concentration, but not to the concentration of initiator.

Further insight into the effect and nature of crosslinking results from a variety of characterization techniques. From calorimetry, we determine that crosslinking with divinylbenzene increases the glass transition temperature of polystyrene beads, as crosslinking inhibits chain motion. At 10% by weight of divinylbenzene, the molecular weight between crosslinks should approximate 1200. The concentration of oligomeric free radicals on the bead surface, at 100% conversion, must be extremely small, as no oxygen or sulfur was detected on the bead surface by X-ray photoelectron spectroscopy. Moreover, elemental analysis of the bulk beads correspond to "pure" polystyrene. To some extent, the oxidative stability of the polystyrene beads depends on the nature of end group from the initiator. Thus, chains ending in hydroxyl groups, from hydrogen peroxide, appear to be more stable than polystyrene terminated with sulfate, from potassium persulfate.

The degree of swelling of crosslinked beads, inferred from dynamic light scattering in tetrahydrofuran, corresponds to a crosslink density of 1.5% for beads synthesized with 4.5 mole percent divinylbenzene. The factor of three disagreement may suggest that the efficiency of crosslinking is low. Since divinylbenzene is a more reactive monomer than styrene, it is preferentially reacted in early stages of polymerization [50]. Here, the formation and loss of surface active oligomeric free radicals may result in a decreased effective concentration of crosslinker.

CONCLUSIONS

Monodisperse crosslinked polystyrene beads of varied size and crosslink density are prepared by emulsion copolymerization of styrene and divinylbenzene in the absence of emulsifier using various reactor designs. The rate of conversion increases with increasing temperature and initiator concentration and decreasing monomer concentration. The reaction must be kept free of oxygen to permit an appropriate rate of polymerization for producing monodisperse beads in high yield. Particle sizes were most sensitive to polymerization temperature and decreased from 800 to 200 nm on raising the polymerization temperature from 60 to 95°C. The effect of decreasing the overall monomer content was to limit the ultimate growth of the beads. The glass transition temperature of the polystyrene beads increased from 104.4 to 133°C by the inclusion of up to 10% by weight of divinylbenzene. From elemental analysis and X-ray photoelectron spectroscopy, the bulk and surface of the beads are, essentially, pure polystyrene. However, the thermal stability of the beads is sensitive to the nature of the end group from the initiator on the polystyrene chain. The crosslink density derived from the degree of swelling was about one third that expected from stoichiometry.

We suggest the following mechanism of polymerization. Free radicals from the initiator are formed in the aqueous phase and, at the beginning of reaction, initiate polymerization by reacting with monomer dissolved in water. At early stages of reaction, "micelles" are formed by the alignment of oligomeric free radicals, containing polar end groups from the initiator. The proximity of these radicals probably leads to some loss of radical activity by reaction. Polymerization continues in the micelles, as oligomeric free radicals or free radical initiator fragments enter micelles, swollen with monomer. At a very early stage of reaction, the number of growing particles is fixed and the beads increase in size as radicals enter the monomer swollen polymer particles. Since the "emulsion" polymerization is emulsifier poor, surface active oligomeric radicals, formed in the aqueous phase, are adsorbed onto the surface of growing particles. With increasing particle size, the

free radicals are further separated, and persist for longer periods of time. Thus, the mean life time of growing chains and the resultant molecular weights increase with conversion. We suggest that oligomeric free radicals adsorb onto the surface of growing particles and act to either initiate new polystyrene chains or terminate growing polystyrene chains.

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Table 1.

Effect of Initiator Concentration on Particle Size

Weight Fraction Divinylbenzene	Initiator Concentration		
	0.845	1.690	3.380×10^{-3} mol/dm^3
0%	409 nm	422 nm	485 nm
1.0	430	425	454

Table 2.

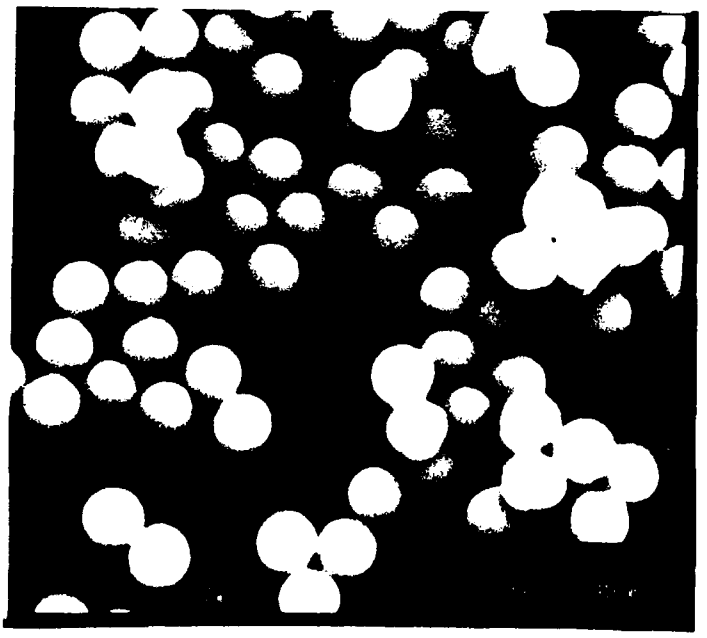
The Glass Transition Temperature (Tg)

of Crosslinked Polystyrene Beads

Weight Fraction Divinylbenzene	Tg
0%	104.4°C
1	107.1
2	110.2
5	112.2
10	133

List of Figures

A



B

FIGURE 1

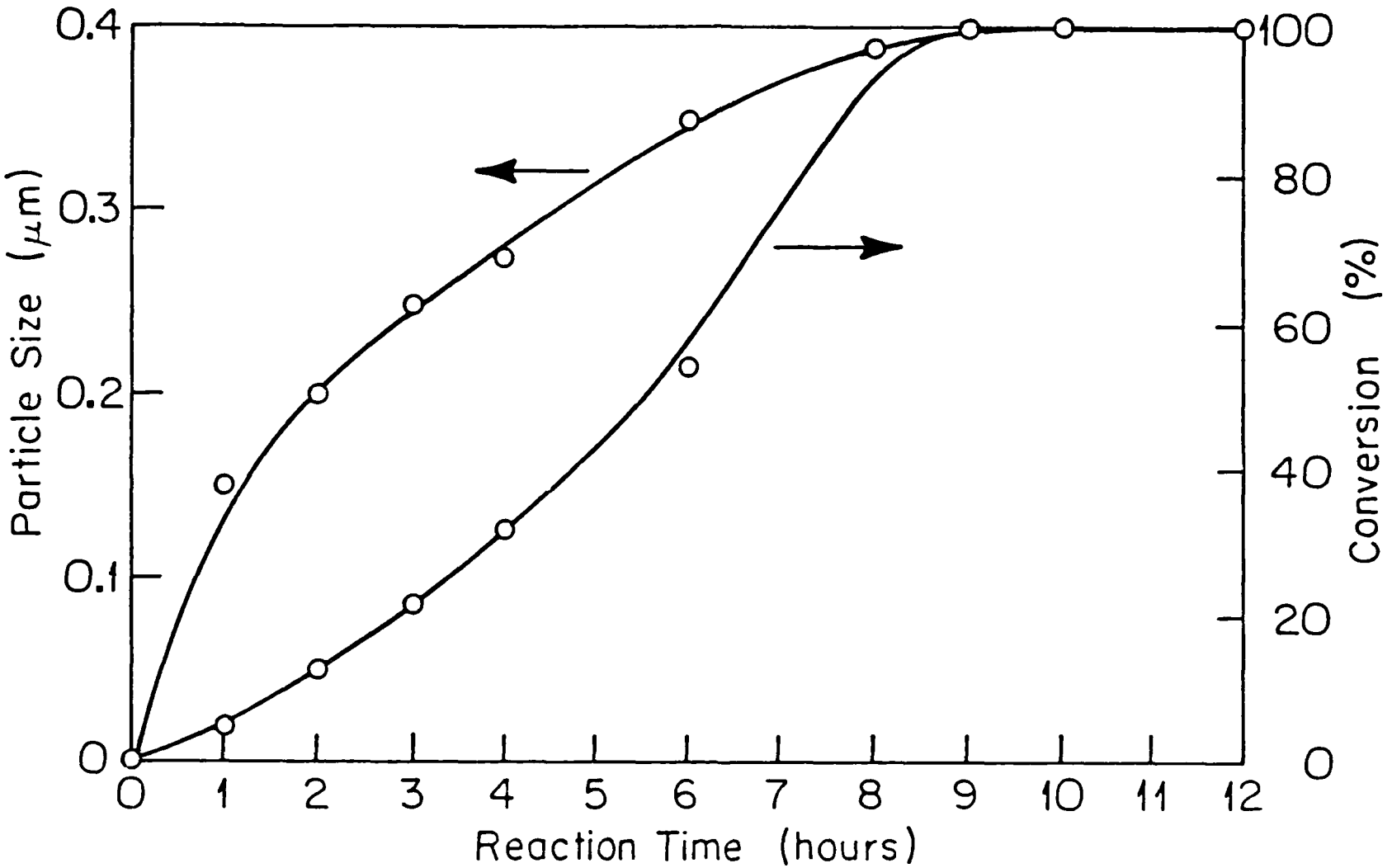

0.4
0.3
0.2
0.1
0
Particle Size (μm)
100
80
60
40
20
0
Conversion (%)
0 1 2 3 4 5 6 7 8 9 10 11 12
Reaction Time (hours)

FIGURE 2

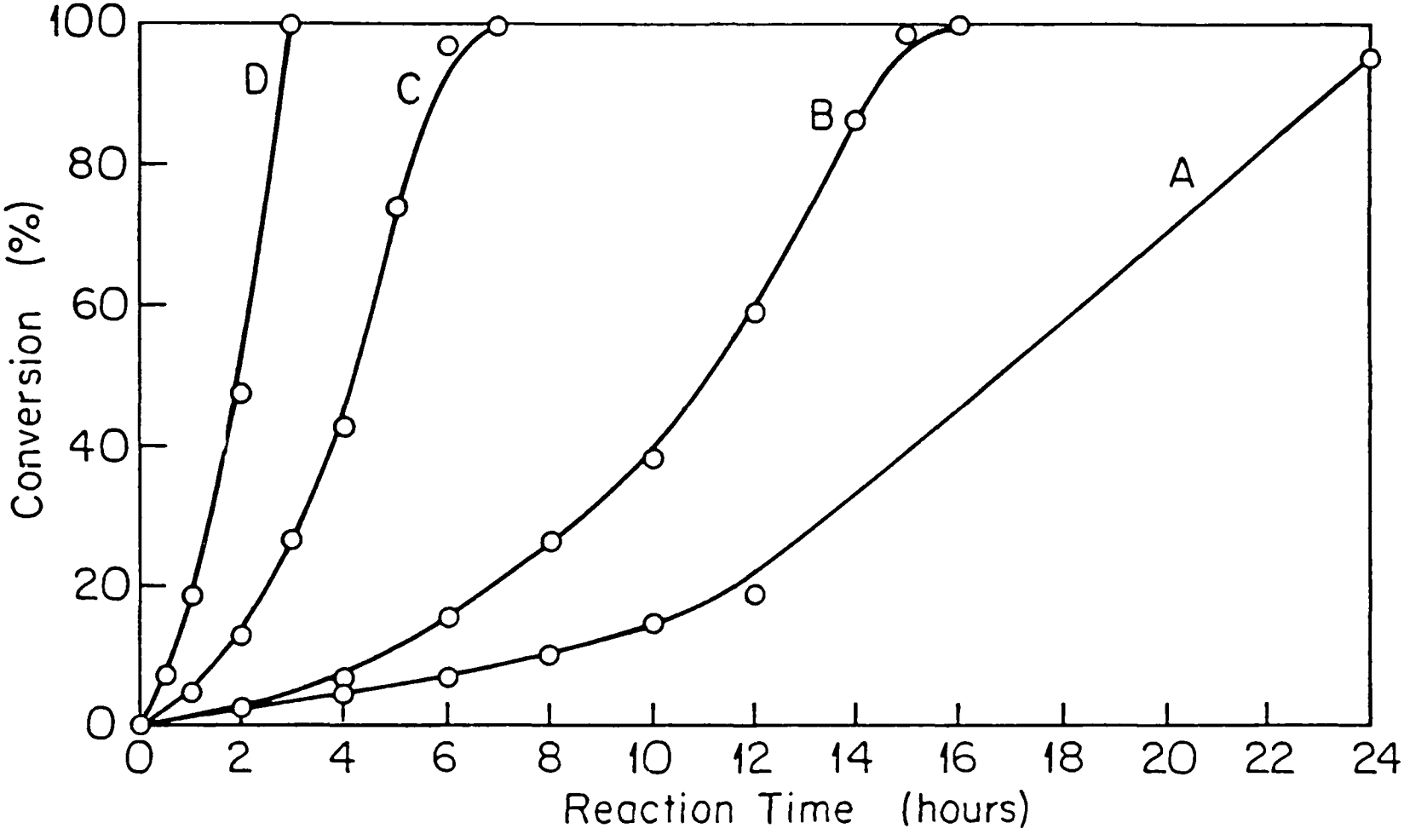

100
80
60
40
20
0
Conversion (%)
D
C
B
A
0
2
4
6
8
10
12
14
16
18
20
22
24
Reaction Time (hours)

FIGURE 3

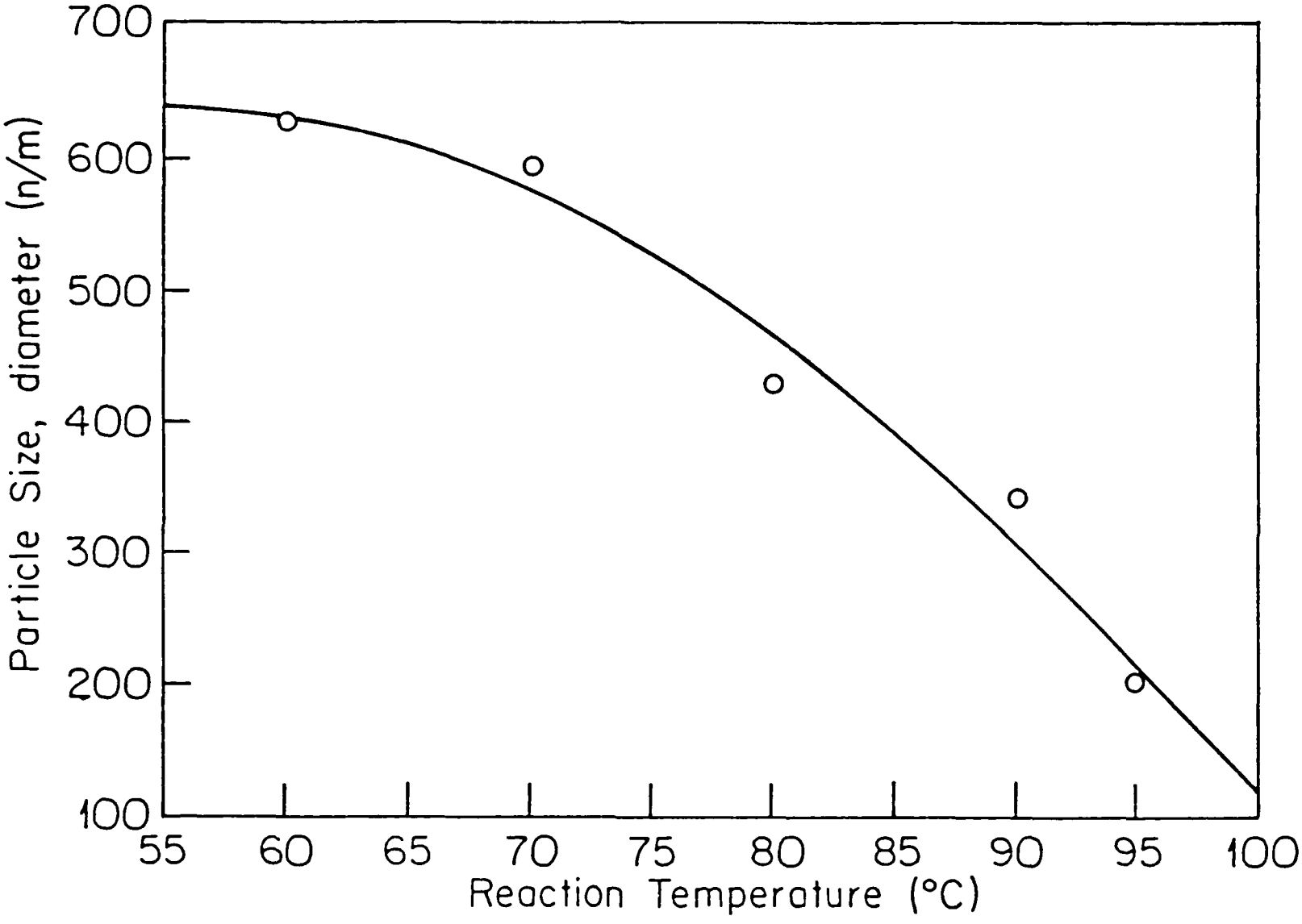

700
600
500
400
300
200
100
Particle Size, diameter (n/m)
55
60
65
70
75
80
85
90
95
100
Reaction Temperature (°C)

FIGURE 4

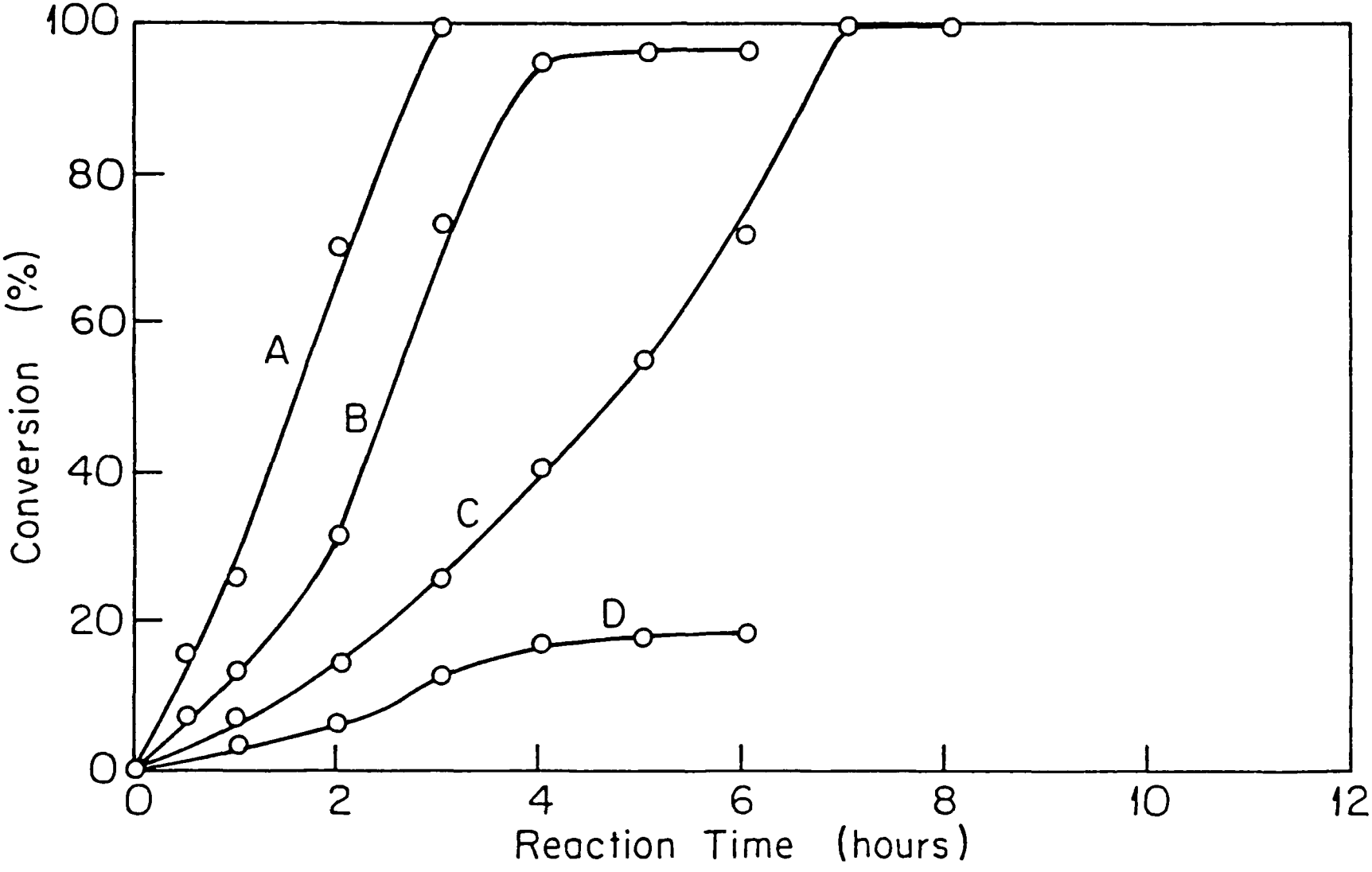

100
80
60
40
20
0
Conversion (%)
A
B
C
D
0
2
4
6
8
10
12
Reaction Time (hours)

FIGURE 5

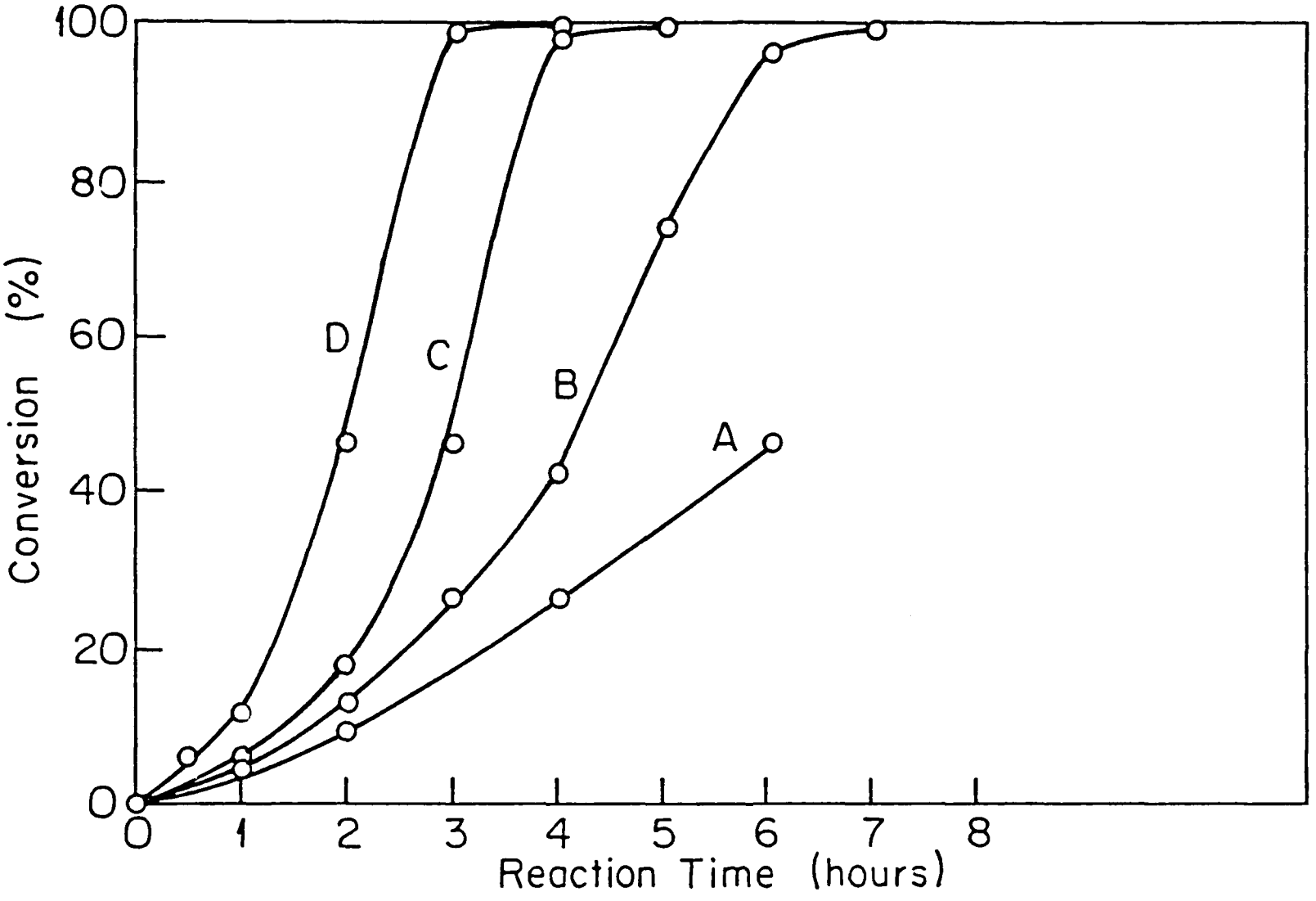

100
80
60
40
20
0
Conversion (%)
D
C
B
A
0
1
2
3
4
5
6
7
8
Reaction Time (hours)

FIGURE 6

DL/1113/89/1

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